

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 209 189 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

29.05.2002 Bulletin 2002/22

(51) Int Cl:7: **C08K 3/34, C08J 9/00**

(21) Application number: **01307254.1**

(22) Date of filing: **28.08.2001**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

• **Wu, Jin Huang**

Norristown, PA 19403 (US)

• **Crooker, Richard M.**

Fogelsville, PA 18051 (US)

(30) Priority: **28.11.2000 US 723858**

(71) Applicant: **Atofina Chemicals, Inc.**

Philadelphia, PA 19103-3222 (US)

(74) Representative: **Stoner, Gerard Patrick et al**

MEWBURN ELLIS

York House

23 Kingsway

London WC2B 6HP (GB)

(72) Inventors:

• **Kresta, Jiri E.**

Warren, MI 48092 (US)

(54) **Foam polymer/clay nanocomposites**

(57) Polymer foams containing nanoclay are provided, the foams having improved properties such as thermal insulation values.

EP 1 209 189 A1

Description

BACKGROUND

[0001] This invention relates to polymer foams containing nanoclay, more particularly to improvements in the properties of polymeric foams by dispersing nanoclay into the polymer foam compositions.

[0002] CFC (chlorofluorocarbon) foam blowing agents such as CFC-11 and CFC-12 provide rigid foams with excellent insulation properties, dimensional stability and fire performance. The use of CFCs has been phased out, however, because they are considered to be detrimental to the ozone layer. The blowing agent alternatives now in use for polymer foams, HCFCs (hydrochlorofluorocarbons), HFCs (hydrofluorocarbons) and HCs (hydrocarbons), generally can not achieve foams having similar properties. For example, the insulation properties are generally poorer because the alternative blowing agents have higher thermal conductivity than CFCs.

[0003] It would therefore be useful to provide the industry with a means of improving polymer foams, especially in terms of insulation values.

BRIEF SUMMARY OF THE INVENTION

[0004] Polymer foam compositions, such as polyurethane foam compositions, are provided which comprise up to about 10 weight % of nanoclay dispersed therein, based on total polymer weight, as well as the resulting polymer foams and the method of making them.

DETAILED DESCRIPTION

[0005] We have found that integration of nanoclay into polymer foam compositions gives useful results. We note that the foams' thermal insulation properties may be improved, (in terms of initial and/or aged k-factors). Also, foams can be made with a fine cell structure, believed to result from the nanoclay acting as a nucleating agent in the foam process. A slow aging rate of the foams suggests that the nanoclay can act as a gas barrier reducing the infusion of air into the foam cells and diffusion of the blowing agents out of the foam cells.

[0006] Nanoclays (nanosized clays) are plate-like materials, the clay mineral being generally selected from smectite, vermiculite and halloysite clays. The smectite clay in turn can be selected from montmorillonite, saponite, beidellite, nontronite, hectorite and mixtures thereof. A preferred clay mineral is the montmorillonite clay, a layered aluminosilicate. The nanoclay platelets generally have a thickness of about 3-1000 Angstroms and a size in the planar direction ranging from about 0.01 micron to 100 microns. The aspect ratio (length versus thickness) is generally in the order of 10 to 10,000. These clay platelets are separated by a gallery, a space

between parallel layers of clay platelets containing various ions holding platelets together. One such material is Cloisite® 10A (available from Southern Clay Products), its platelets having a thickness of about 0.001 micron (10 Angstroms) and a size in the planar direction of about 0.15 to 0.20 micron.

[0007] The invention is applicable to both thermoset and thermoplastic polymer foams. Thermoset polymers include polyurethane, polyisocyanurate and phenolic resins, while thermoplastics include polystyrene, polypropylene, polyethylene and polyvinyl chloride resins.

[0008] Any conventional blowing agent can be used, such as HFCs, HCFCs, HCs or mixtures thereof. HCFC-141b (1,1-dichloro-1-fluoroethane) is illustrated in the example below. Blowing agent quantities may be conventional.

[0009] The nanoclay should be dispersed uniformly in one or more components of the polymer foam composition. This may be done by conventional techniques such as milling or extruding. Or, as in the example below, the nanoclay can be dispersed into the blowing agent using an ultrasonic water bath.

[0010] The amount of nanoclay generally ranges from about 0.01 part to about 10 parts of 100 parts by weight of total (polymer) resin.

[0011] The other components of the foam formulations may be those which are conventionally used, which components and their proportions are well known to those skilled in the art.

[0012] The practice of the invention is illustrated in more detail in the following non-limiting example in which polyurethane foam was made without and with 0.2 part Cloisite® 10A. The two formulations used (each having an Iso Index of 264) each contained 167.9 parts Papi 27, a polymeric methane diphenyl diisocyanate (polyMDI) available from Dow Chemicals; 100 parts T-2541, a polyester polyol having a hydroxyl number of 240 available from Kosa; 3 parts Dabco TMR-4, a trimerization catalyst available from Air Products; 3 parts of B-8433, a polysiloxane polyether copolymer surfactant available from Goldschmidt Chemical Corporation; 0.5 part water; and 40 parts 141b blowing agent; all parts are by weight.

[0013] For the foam without nanoclay, B-side materials (polyol, water, 141b, catalyst and surfactant) were mixed in a container, followed by addition of the A-side (polyMDI). The mixture was vigorously stirred and poured into a box.

[0014] For the foam with nanoclay, B-side materials (polyol, water, catalyst and 50% of the surfactant) were mixed in one container and A-side materials (polyMDI, 50% of the surfactant, Cloisite® 10A dispersed in a portion of the 141b, and the remainder of the 141b) were mixed in a second container, after which the two sides were mixed together, vigorously stirred and poured into a box.

[0015] In order to compare the relative thermal conductivity of the foams, k-factor tests were conducted ac-

according to ASTM-C-518, both initially and after aging at room temperature for three months. The foam without nanoclay gave initial and aged k-factors (in Btu.in/ft².h.F) of 0.139 and 0.193, while the foam with nanoclay gave initial and aged k-factors of 0.135 and 0.182, showing that the nanoclay results in better initial insulation values and that the improvement increases on aging.

Claims

1. A polymer foam composition containing up to about 10 weight % of nanoclay dispersed therein, based on the total weight of polymer.
2. A polymer foam made from the composition of Claim 1.
3. A polyurethane foam composition containing up to about 10 weight % of nanoclay dispersed therein, based on the total weight of polyurethane.
4. A polyurethane foam made from the composition of Claim 3.
5. A method of making a polymer foam comprising mixing a polymer composition (polymer or polymer precursors) with blowing agent and setting or curing the polymer composition when foamed by the blowing agent,
characterised by the use of nanoclay in the polymer composition, at up to 10wt%.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 7254

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 00 47657 A (FIBIGER RICHARD F ;BARGER MARK A (US); SUH KYUNG W (US); TUNG HARV) 17 August 2000 (2000-08-17) * abstract; claim 1; example 2 * * page 5, line 4 - line 13 * * page 5, line 26 - page 6, line 9 * ----	1,2,5	C08K3/34 C08J9/00
Y	EP 0 388 952 A (UNION CARBIDE CHEM PLASTIC) 26 September 1990 (1990-09-26) * abstract; claim 1 * * page 4, line 52 - line 55 * ----	3,4	
Y	PATENT ABSTRACTS OF JAPAN vol. 006, no. 127 (C-113), 13 July 1982 (1982-07-13) & JP 57 051728 A (TOSHIBA CORP), 26 March 1982 (1982-03-26) * abstract * -----	3,4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08K C08J
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 31 October 2001	Examiner Schütte, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 30 7254

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-10-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 0047657	A	17-08-2000	AU	3489800 A	29-08-2000
			WO	0047657 A2	17-08-2000
EP 0388952	A	26-09-1990	US	5094775 A	10-03-1992
			AT	146203 T	15-12-1996
			AU	639689 B2	05-08-1993
			AU	5212490 A	27-09-1990
			CA	2012848 A1	22-09-1990
			DE	69029337 D1	23-01-1997
			DE	69029337 T2	10-04-1997
			EP	0388952 A2	26-09-1990
			ES	2095845 T3	01-03-1997
			GR	3021996 T3	31-03-1997
			NZ	233023 A	26-07-1991
			PH	26999 A	01-02-1993
JP 57051728	A	26-03-1982	JP	1387632 C	14-07-1987
			JP	61054332 B	21-11-1986

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)